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THE INFLUENCE OF SUBSTRATE CONFIGURATION AND TEMPERATURE ON THE EPITAXIAL GROWTH OF GERMANIUM FILMS

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ABSTRACT

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The formation of epitaxial deposits of Ge on heated substrates of CaF_2, BaF_2, MgO, and $SrMoO_4$ has been investigated by reflection electron diffraction at six different temperatures ranging from 410° to 920° C. The effect of surface topography was also studied by depositing the films on both cleaved and polished CaF_2 substrates and on cleaved and etched MgO substrates. True epitaxial growth of the Ge films on CaF_2 substrates was observed at temperatures of 590° C and above for the cleaved (111) faces but only at 920° C for the polished (111) faces. Formation of single crystal deposits on the polished surfaces was shown to be related to the annealing of the substrate during deposition of the film. At all other temperatures, polycrystalline or partially oriented deposits were obtained. For the (111) cleavage plane of BaF_2, epitaxial growths with pronounced [111] twinning formed only at 920° C. Only polycrystalline films were obtained with MgO and $SrMoO_4$ substrates at all temperatures employed.

INTRODUCTION

The conditions that influence the epitaxial growth of numerous thin metallic and alkali halide films have been extensively investigated, and this work has been reviewed by Pashley[1] and Sloope[2]. The conditions under which epitaxial films of homopolar materials such as Ge and Si may be deposited are not as well understood. No epitaxial growth has been reported for Ge films on amorphous substrates[3,4], but deposition on Ge single crystals results in epitaxial growth at high temperatures[5-9]. Deposition on crystalline substrates has also been reported by several authors. Crystalline films are formed on NaCl and Al_2O_3[10,11] at temperatures above 380° C and show increasing orientation with increasing temperature. The most successful efforts to obtain epitaxial deposits

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of Ge have been made using CaF_2 as the substrate[2,12,13]. Marucchi and Nifontov[12] obtained twinned single crystals of Ge on the (111) cleavage plane of CaF_2 above 540° C. Nifontov[14] reports similar results. Via and Thun[15] obtained twinned and cracked films when deposits were formed on cleavage faces of CaF_2, but good crystals formed on polished surfaces. The (100) surfaces gave films with lesser order.

Previous work in this laboratory[16] observed the beginnings of single crystal formation on mechanically polished (110) planes of CaF_2 at 915° C. Lower temperatures gave lesser amounts of orientation. Sloope and Tiller[13] have reported that single crystal formation on cleaved CaF_2 depends on both the temperature and the rate of deposition. Cleaved NaCl, NaF, and MgO were also employed as substrates by these authors, but they were unable to secure single crystals of Ge on any of these materials, although some preferential orientation was observed with all.

The work described herein was undertaken in order to extend the knowledge of the conditions necessary for the formation of epitaxial deposits of Ge. The germanium films were deposited at a constant rate on four

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substrates (CaF_2, BaF_2, MgO, and $SrMoO_4$) at temperatures ranging from 400° to 920° C.

The lattice parameters of the substrates and the percentage misfit[a] for the Ge films are given in the following table:

TABLE I. - PERCENTAGE MISFIT OF GERMANIUM FILMS FOR VARIOUS SUBSTRATES.

Substrate	Lattice constants		Percentage misfit
	a_o	c_o	
Ge	5.66	---	---
CaF_2	5.46	---	+3.7
BaF_2	6.20	---	-8.7
MgO	4.21	---	+34.4
$SrMoO_4$	5.39	12.02	+5.0 along [100] or [010]
			-5.8 along [001] (for two lattice units)

The effect of surface topography was studied by using both cleaved and polished CaF_2 substrates and cleaved and etched MgO substrates. Only cleaved surfaces were employed for BaF_2.

EXPERIMENTAL

The substrates employed were single crystal plates of CaF_2, MgO, BaF_2, and $SrMoO_4$. The fluorite plates, as supplied had been cleaved and then polished mechanically on one side to a plate-glass surface. The

[a]The percentage misfit is defined by Pashley[1] as 100(b-a)/a where a and b are the corresponding network spacings in the substrate and the overgrowth, respectively.

resulting orientation was checked by X-ray diffraction to assure that the (111) plane was parallel to the surface. These polished CaF_2 substrate plates were washed with acetone and distilled water prior to use. The BaF_2 plates were also prepared by cleavage on the (111) plane. Both cleaved and cut surfaces were employed with the MgO. For MgO, the cleavage plane is (100); the (111) and (110) plates were prepared by cutting, and all three planes were subsequently etched in boiling H_3PO_4 for 1 min. For the $SrMoO_4$ the (100) plane was cut, polished, and annealed at 1100° C until electron diffraction patterns showed sharp Kikuchi lines. The orientation was also checked by X-ray diffraction.

The Ge films were prepared by vacuum evaporation in a conventional bell jar at pressures ranging from 10^{-4} to 10^{-5} mm Hg. The rate of evaporation of the Ge was constant at about 1500 Å/min (or 25 Å/sec). The Ge was taken from an ingot of the material previously employed[16]. It was evaporated from a Ta boat onto the substrate plates, which in turn were clipped to the underside of a Ta strip. Both the boat and the strip were resistance heated. The temperature of the strip was measured by a thermocouple welded to the strip, and the temperature of the substrate was assumed equal to that of the strip. Films approximately 3000 Å thick were prepared at six different temperatures ranging from 410° to 920° C on the fluorite substrates, from 590° to 920° C on BaF_2, and from 590° to 920° C on MgO and at only one temperature (920° C) for the $SrMoO_4$.

The crystalline nature of the films was studied by reflection electron diffraction with an accelerating potential of 36 kv.

RESULTS

The diffraction results obtained on the films formed at varying temperatures and on the substrates employed are briefly given in table II. Data previously obtained[16] for Ge on polished (110) CaF_2 is included for reference.

TABLE II. - ELECTRON DIFFRACTION PATTERNS OF GERMANIUM FILMS

Substrate	Surface	Substrate pattern	Temperature, °C					
			920	790	700	590	500	410
CaF_2	(111) cleaved	Kikuchi lines	Spots	Diffuse spots and twinning	Diffuse spots and twinning	Diffuse spots and twinning	Rings and diffuse spots	Diffuse rings
	(111) polished	Amorphous	Diffuse spots (doublets)	Arcs and spots	Arcs	Diffuse rings	Diffuse rings	-------
	(110) polished	Amorphous	Diffuse spots and rings	(760° C) Rings and spots	---- ----	(575°C) Diffuse rings	(470° C) Amorphous	----
BaF_2	(111) cleaved	Kikuchi	Spots and twinning	Arcs	Arcs	Amorphous	---------	-------
MgO	(111) Etched	-------	Rings	Rings	Rings	Rings	---------	-------
	(110) Etched	-------	Rings and spots	Arcs	Rings and arcs	-------	---------	-------
	(100) Etched	Spots	Rings and spots	Rings and arcs	----	-------	---------	-------
	(100) Cleaved	-------	Rings and spots	Rings	-------	-------	---------	-------
$SrMoO_4$	(100) Annealed	Kikuchi lines	Rings	-------	-------	-------	---------	-------

A. The Effect of Lattice Constant and Surface Configuration on Crystallinity of Ge Films at 920° C

At 920° C, epitaxially grown films of Ge are formed on both cleaved and polished (111) faces of CaF_2 (see fig. 1). The most perfect films (those presenting a Laue pattern of sharp spots and showing only faint evidence of twinning) were formed on the cleaved (111) faces. On the polished faces, a Laue spot pattern was also obtained, but one with rather irregular diffuse spots (some of which were doublets) indicating that perhaps the film was of a mosaic type. In both cases, however, the (111) plane of the Ge was parallel to the surface of the substrate, which is also a (111) plane. The azimuth was $[1\bar{1}0]$. The misfit in this case is +3.7%, and this small amount does not appear to disturb the crystallization of the Ge film.

A comparison of the results on cleaved and polished (111) faces of CaF_2 with those on polished (110) faces[16] may be made to give some indication of the effect of the nature of the substrate on the type of film deposited. On the polished faces, it was difficult to form epitaxial deposits - with only those at 920° C showing appreciable amounts of single crystal formation. Thus the preferred plane for the formation of epitaxial deposits appears to be the (111), and a highly ordered surface gives the best results.

For BaF_2, single crystal Laue patterns were obtained (fig. 2(a)). These included many satellite spots that could be interpreted as arising from multiple twinning within the film from the normal [111] axis. The identification of the spot pattern (fig. 2(a)) and the source of the satellites is indicated by the diagram in fig. 3. Since there is a relatively large negative misfit of -8.7% between the lattice parameters of BaF_2 and Ge, it is possible that the strains introduced in trying to match the substrate lattice may lead to substantial amounts of twinning in the surface film.

Experiments were also performed on varying faces of the MgO substrate: the cleaved (100) plane and the etched (100), (110), and (111) planes. In none of these cases, was a good epitaxial deposit formed, although some evidence of single crystals growing at the expense of the random material was observed (fig. 4). The results on the cleavage plane (100) are similar to those of Sloope and Tiller[13]. The large lattice misfit of +34% probably precludes the formation of any true epitaxial deposits.

Only polycrystalline deposits formed on the $SrMoO_4$ (fig. 2(b)). Here the substrate lattice plane might be expected to match two units of the Ge (100) plane. The misfit in the [010] direction is +5% and in the [001] direction is -5.8% for 2 lattice units. This amount of misfit is less than that of the BaF_2, but no true epitaxy developed in the film, although it might have been expected. It may be possible that the large size of the MoO_4^{--} ion hinders the migration of the Ge atoms and prevents them from forming an ordered layer.

B. Effect of Temperature

Ge films deposited on cleaved CaF_2 at the lowest temperature, 410° C, gave only diffuse rings indicating a polycrystalline deposit consisting of very small crystallites. At 500° C, some single crystals had started to form, as indicated by the spots superimposed on the ring pattern (fig, 5(c)). At 590° C and above, single crystal deposits were obtained. Considerable twinning was observed at 590° C and this decreased in amount until it had nearly vanished at 920° C (figs. 5(a)-(c)). In all cases, the (111) plane of the Ge was parallel to that of the substrate, and the azimuth was $[1\bar{1}0]$.

With polished (111) CaF_2 substrates, increasing order was observed with increasing temperature until epitaxial deposits were obtained at the highest temperature, 920° C (figs. f(d)-(f)). A consideration of the nature of the substrate surface may help to explain the difference between these two sets of samples. Examination of the cleaved substrate by the electron diffraction indicated a highly crystalline surface, which gave Kikuchi line patterns. For the polished (111) surface, only patterns indicating an amorphous layer were obtained. Since the substrate itself lacks order, it is not surprising to find that the Ge films fail to form the desired single crystals. This, however, does not explain the fact that some order does occur at the highest temperatures. A sample of polished CaF_2 substrate was therefore placed in the evaporating unit and held at a temperature of 920° C for 10 min, thus approximating the conditions under which the Ge film is deposited. Electron diffraction pictures of this heated sample were then taken and showed that considerable annealing had resulted, even in this short period. The plate showed that a strong spot pattern developed, that was superimposed on sharply defined rings. Thus it is not surprising that an improvement in the degree of crystallinity of a deposited Ge film should result. The appearance of arcs in the Ge layers at 700° C suggests that some annealing of the substrate surface may occur even at this low temperature.

Additional annealing of the polished CaF_2 for 1 hr at 1025° C resulted in increased order of the substrate surface. The electron diffraction pattern showed strong Laue spots and traces of Kikuchi lines. A Ge film deposited on this annealed substrate at 700° C showed a strong Laue spot pattern, including twinning superimposed on a background of fainter rings. This is an improvement over the polished sample at 700° C, but it is not as good as the film prepared on the cleaved substrate at the same temperature.

Films deposited on cleaved (111) BaF_2 substrates are amorphous at 590° C, but they show increasing amounts of orientation at 700° and 790° C and become single crystals at 920° (see fig. 6). At the highest temperature, large amounts of twinning are observed. This twinning was previously discussed in section A. The lattice misfit in this case is -8.7%, and it clearly hinders the formation of an epitaxial layer, since such layers begin to form on the cleaved CaF_2 at temperatures as low as 590° C.

With MgO, no epitaxial layer was formed at any of the temperatures employed (see fig. 7). Here again, the very large misfit of +34% in the lattice parameters is probably responsible.

SUMMARY

True epitaxial growth of Ge films on the cleaved (111) faces of CaF_2 substrates have been achieved at temperatures of 590° C and above and at 920° C on cleaved (111) faces of BaF_2. At lower temperatures, polycrystalline and partially oriented layers have been obtained.

On the smoothly polished (111) face of CaF_2, single crystal patterns of poor quality were obtained at 920° C, but these were shown to be related to the partial annealing of the substrate at the highest temperature. It appears that no epitaxial deposit will form on a polished (amorphous) CaF_2 surface.

In the case of MgO substrates, polycrystalline films were obtained at all temperatures for etched (111), (110), and (100) planes and cleaved (100) planes of the substrate. It appears that a misfit of +34% is too great to allow the formation of epitaxial deposits.

For $SrMoO_4$, only polycrystalline films were obtained at 920° C.

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FIG. 1. Effect of surface configuration on Ge films deposited on CaF_2 substrates at 920° C.

(a) Cleaved (111).

(b) Polished (111).

FIG. 2. Effect of surface configuration on Ge films deposited at 920° C.

(a) BaF_2 (111).

(b) $SrMoO_4$ (100).

FIG. 3. Ge on cleaved (111) face of BaF_2 at 920° C (Identification of pattern in fig. 2(a)).

FIG. 4. Effect of surface configuration on Ge films deposited on MgO substrates at 920° C.

(a) Etched (110).

(b) Etched (111).

(c) Etched (100)

(d) Cleaved (100).

FIG. 5. Effect of substrate temperature on the deposition of Ge films on CaF_2 substrates.

(a) Cleaved (111) at 920° C.

(b) Cleaved (111) at 700° C.

(c) Cleaved (111) at 500° C.

(d) Polished (111) at 920°C.

(e) Polished (111) at 700° C.

(f) Polished (111) at 500° C.

FIG. 6. Effect of substrate temperature on the deposition of Ge films on BaF_2 (111).

(a) 920° C.

(b) 700° C.

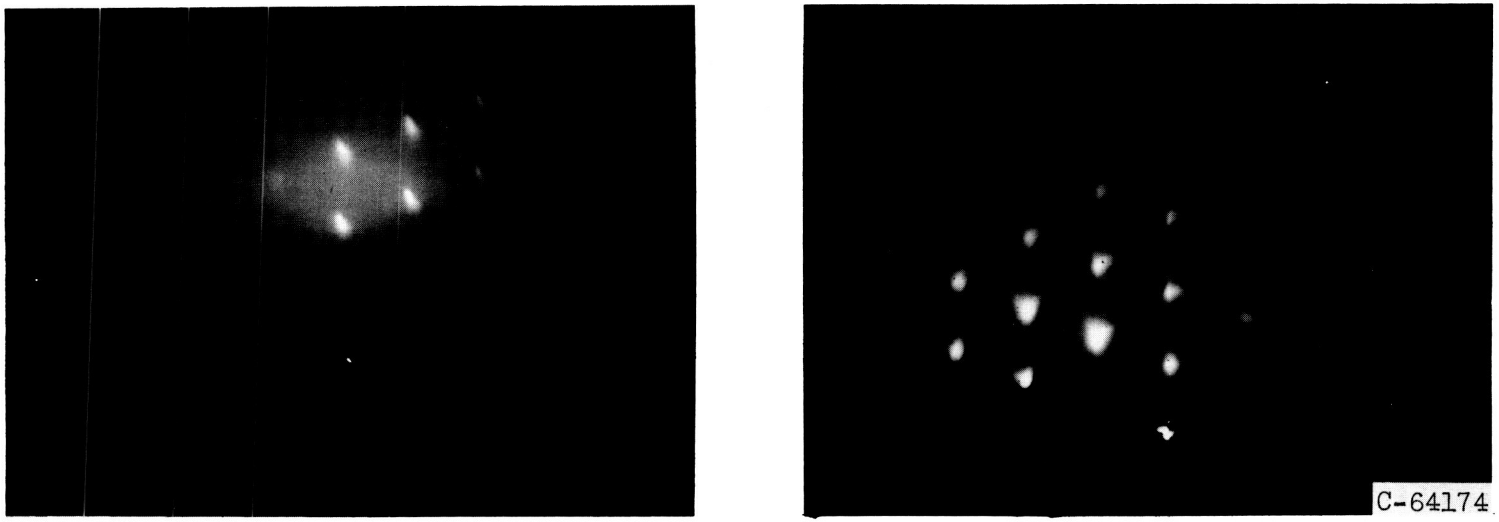
FIG. 7. Effect of substrate temperature on the deposition of Ge films on MgO substrates.

(a) Etched (111) at 920° C.

(b) Etched (111) at 700° C.

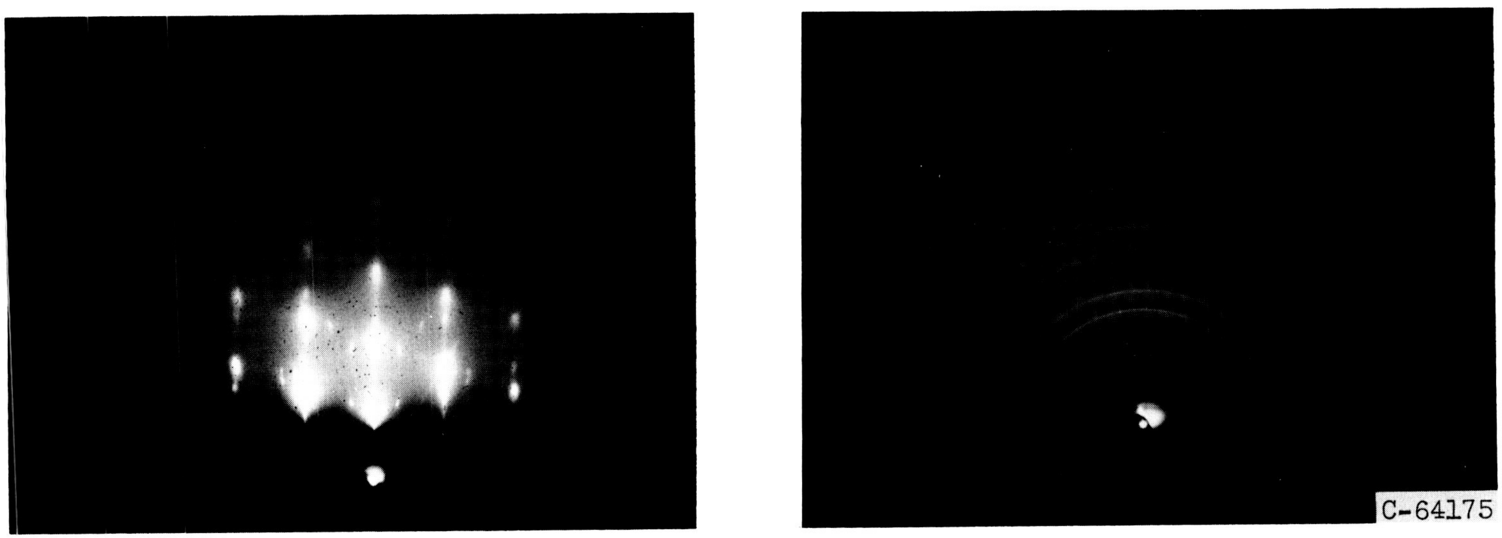
(c) Etched (110) at 920° C.

(d) Etched (110) at 700° C.



(A) (B)

Figure 1



(A) (B)

Figure 2

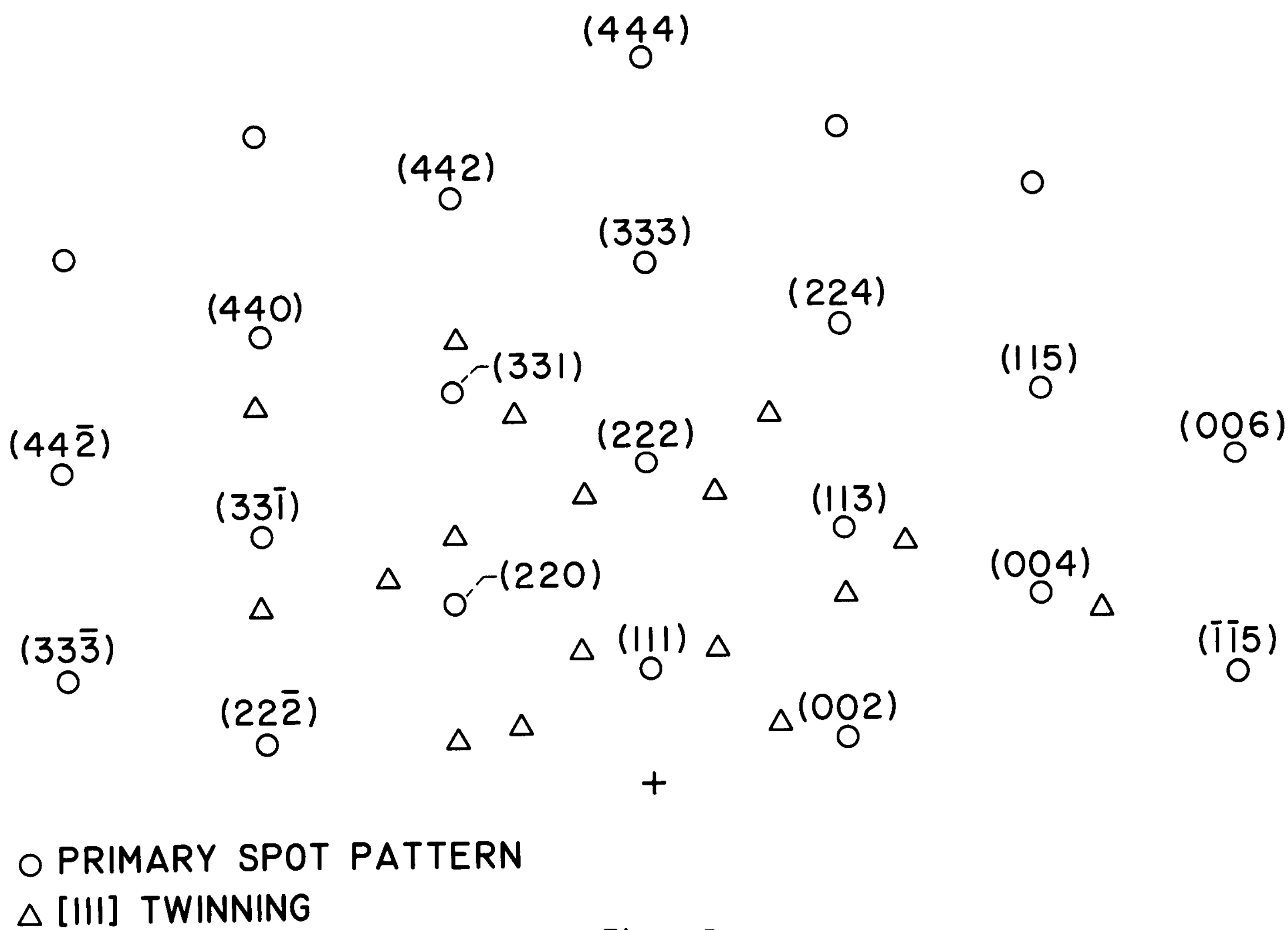

(444)
(442)
(333)
(224)
(440)
(331)
(115)
(44$\bar{2}$)
(222)
(006)
(33$\bar{1}$)
(113)
(220)
(004)
(33$\bar{3}$)
(111)
($\bar{1}\bar{1}$5)
(22$\bar{2}$)
(002)
○ PRIMARY SPOT PATTERN
△ [111] TWINNING

Figure 3

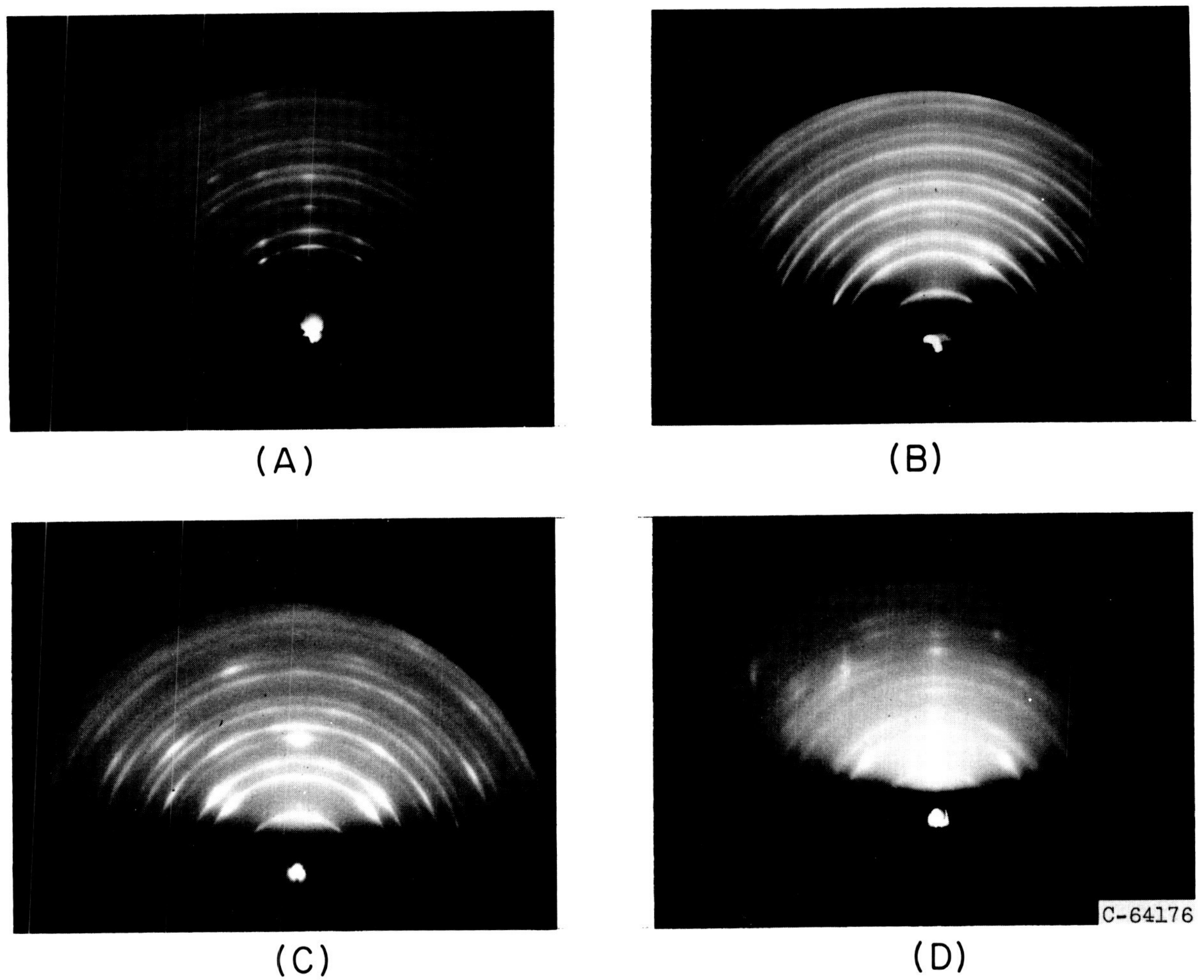


Figure 4

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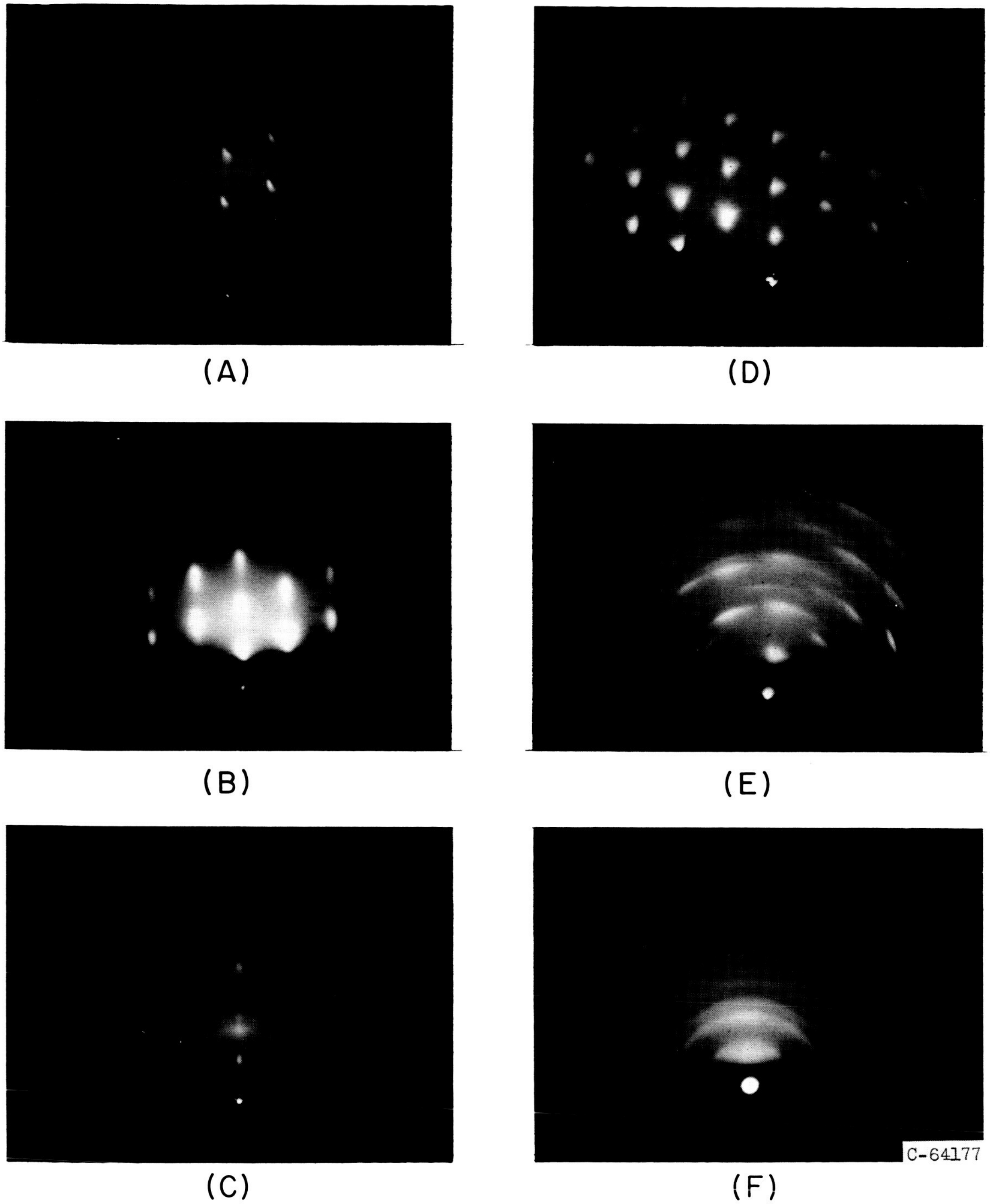
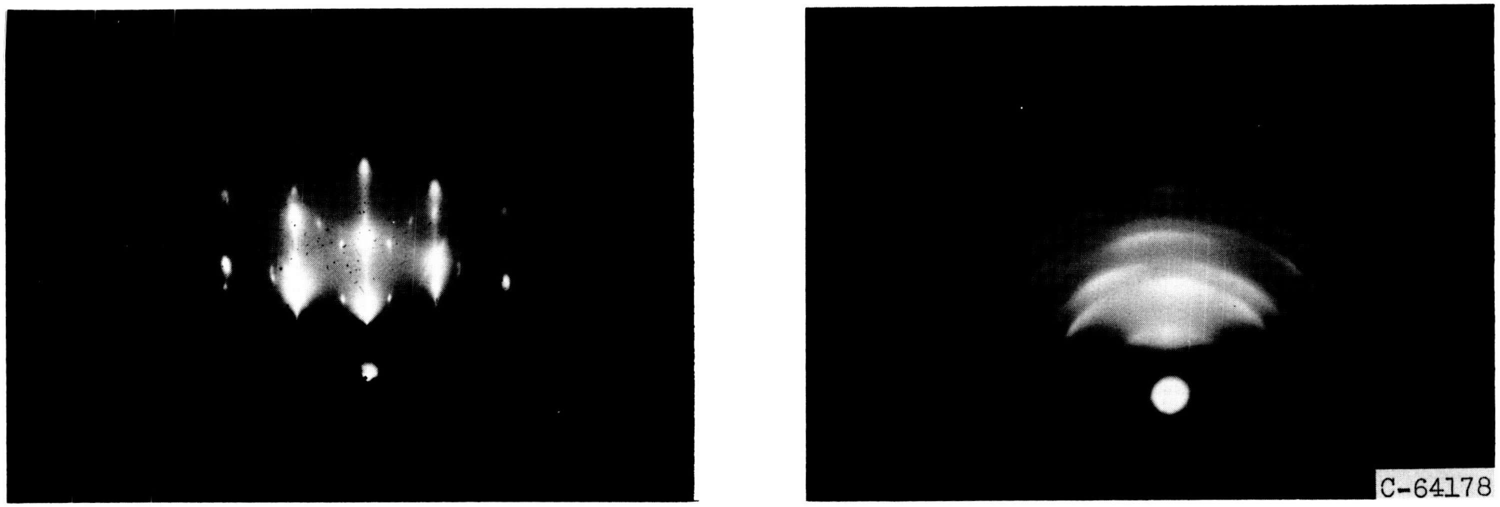
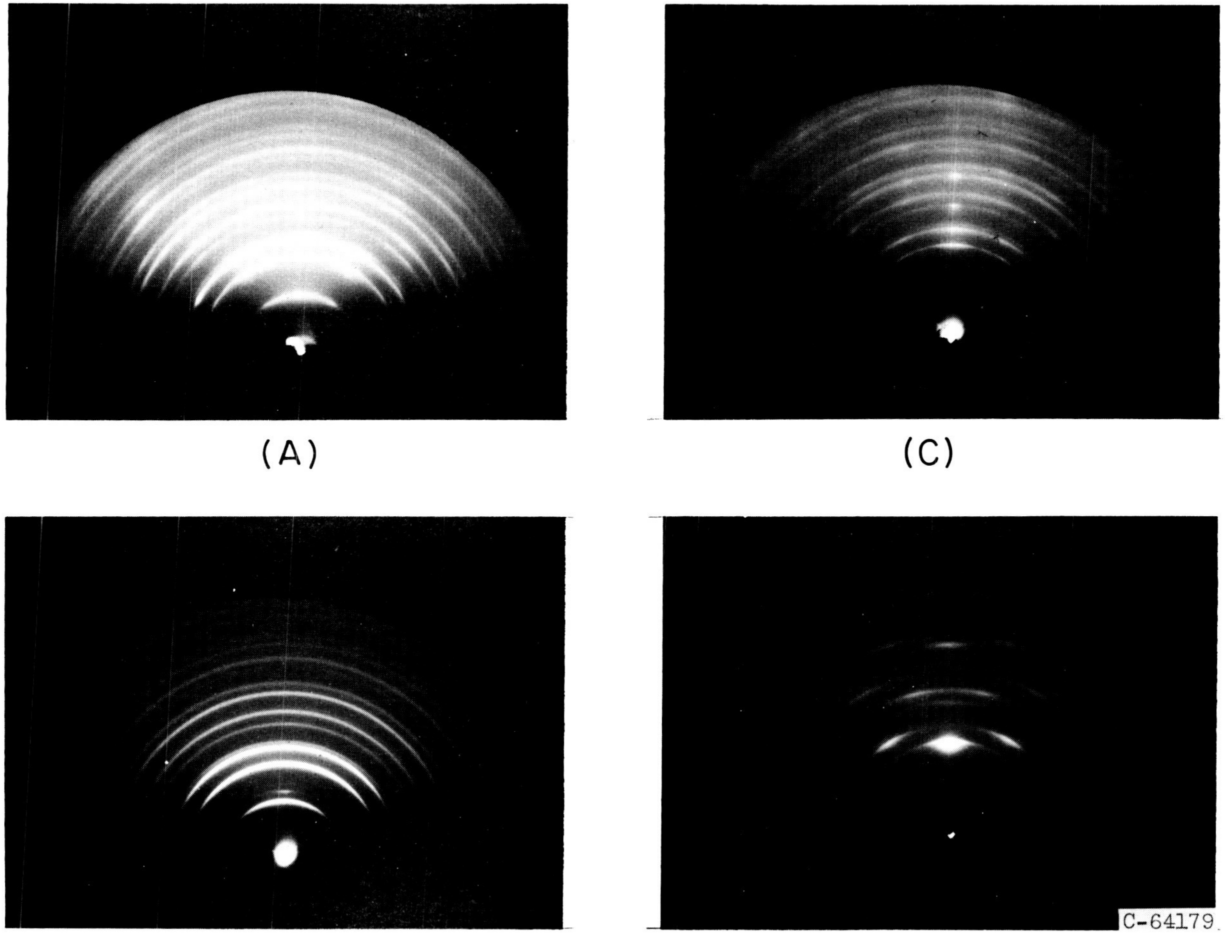


Figure 5



(A) (B)

Figure 6



(A) (C)

(B) (D)

Figure 7

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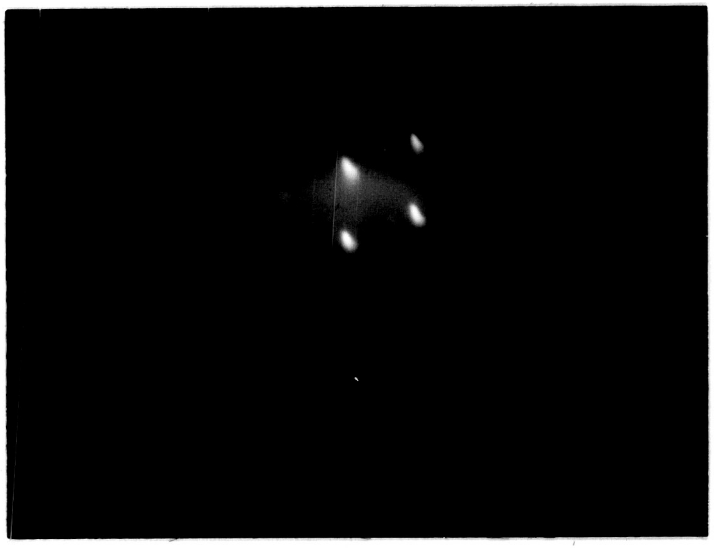
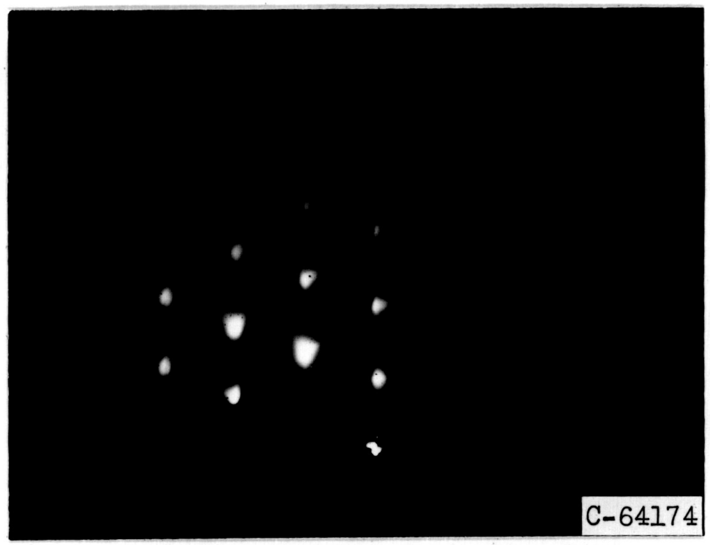


(A)



(B)

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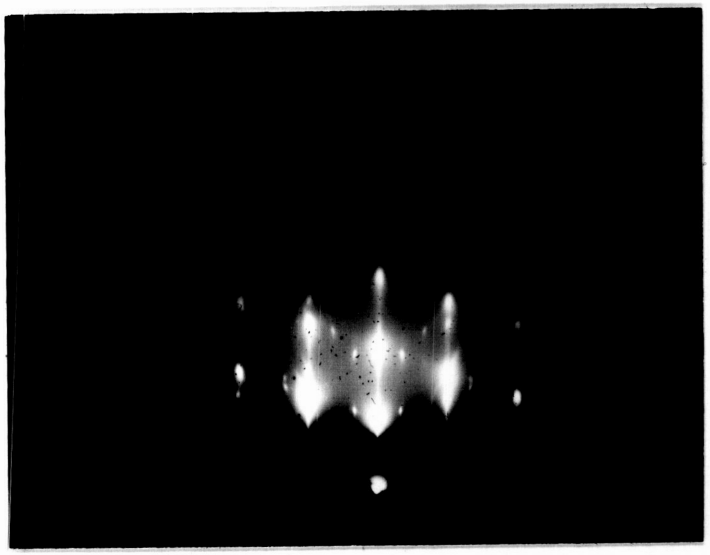

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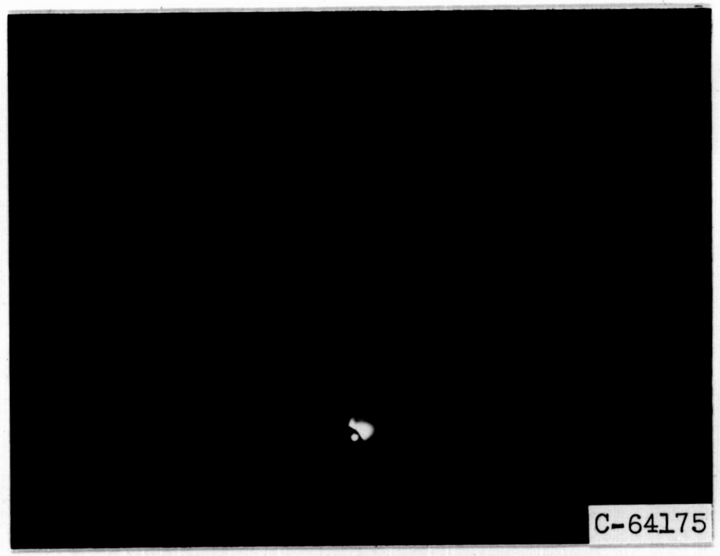

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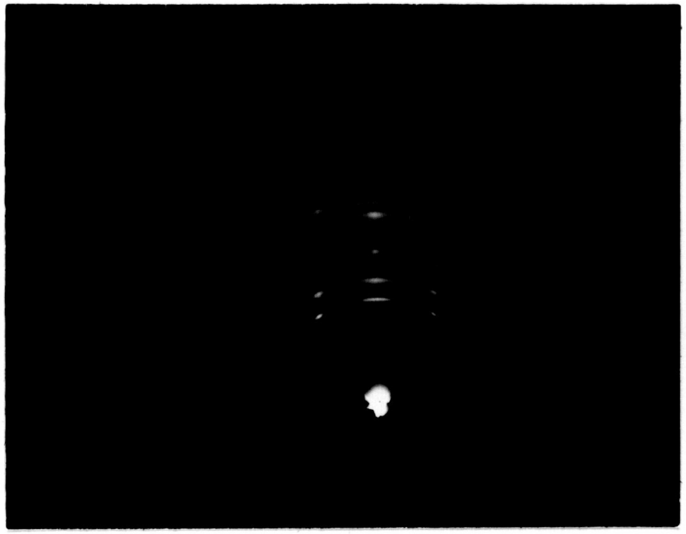

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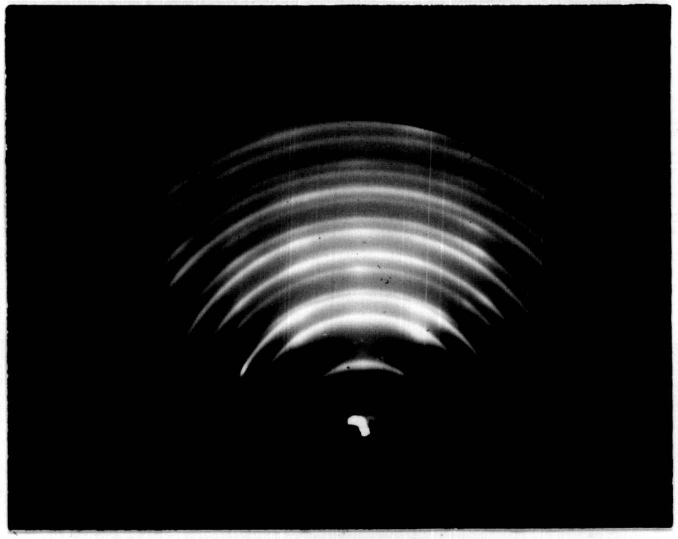

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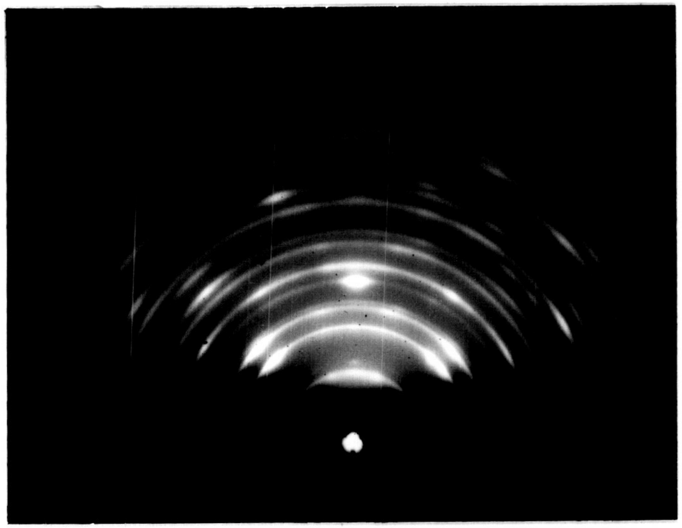

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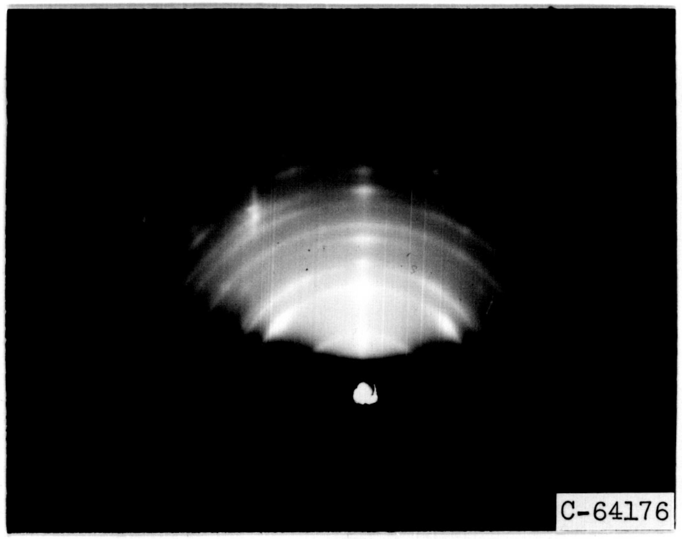

(D)

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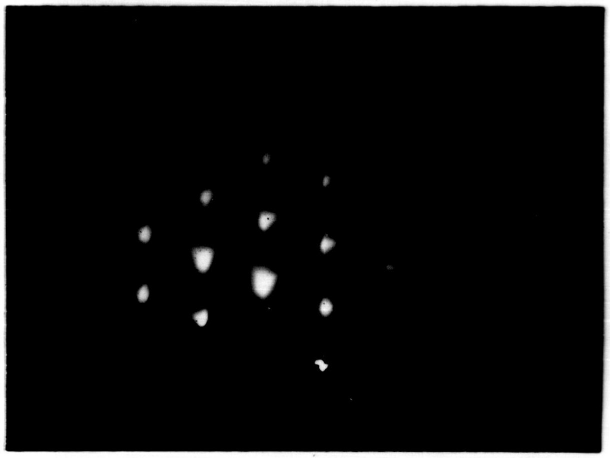
(A)



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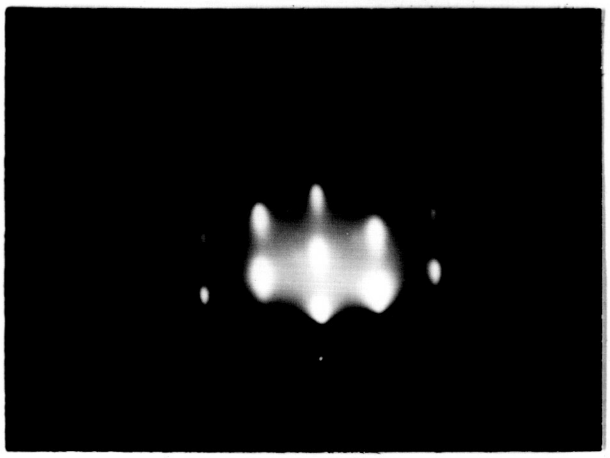

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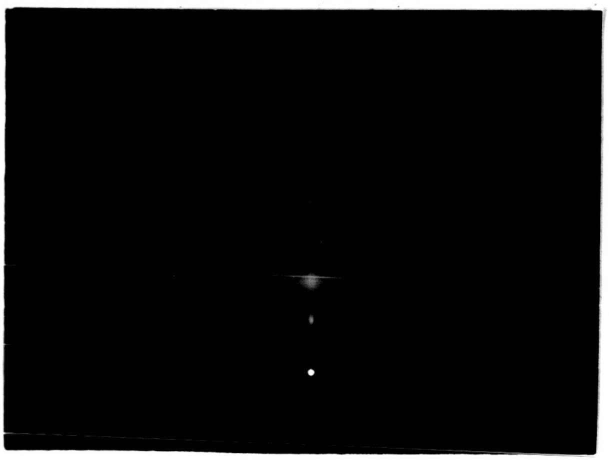
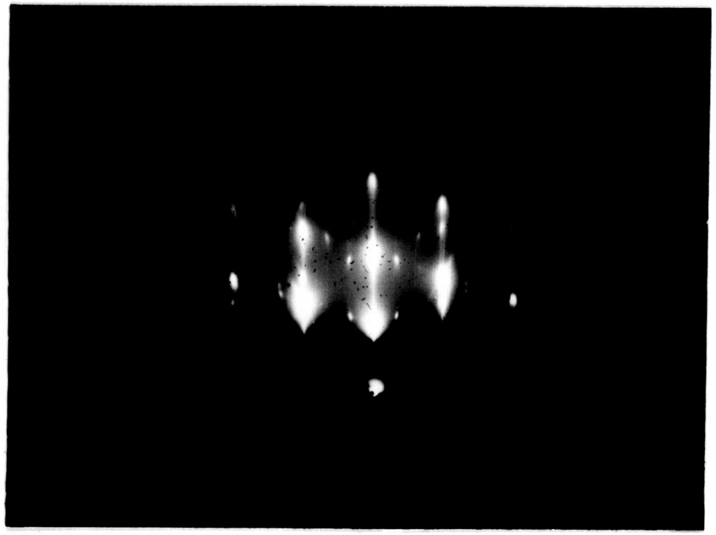
(E)



(C)

(F)



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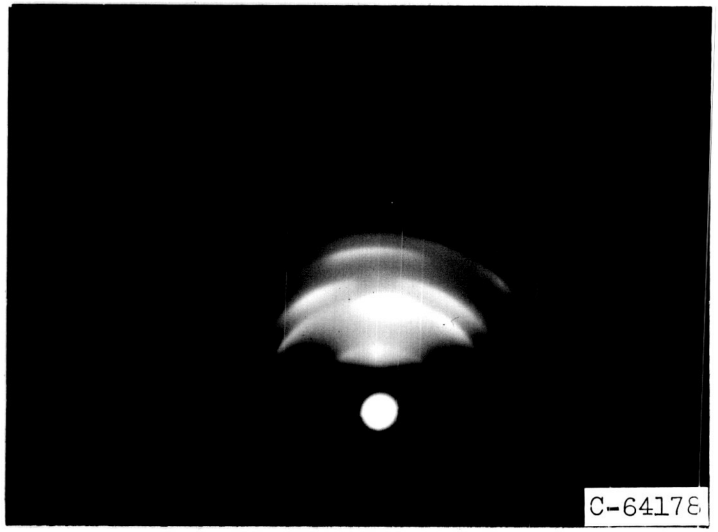

(B)

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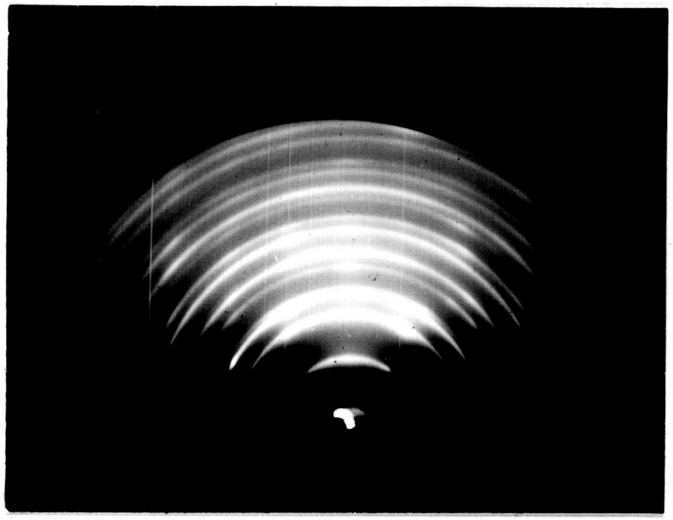

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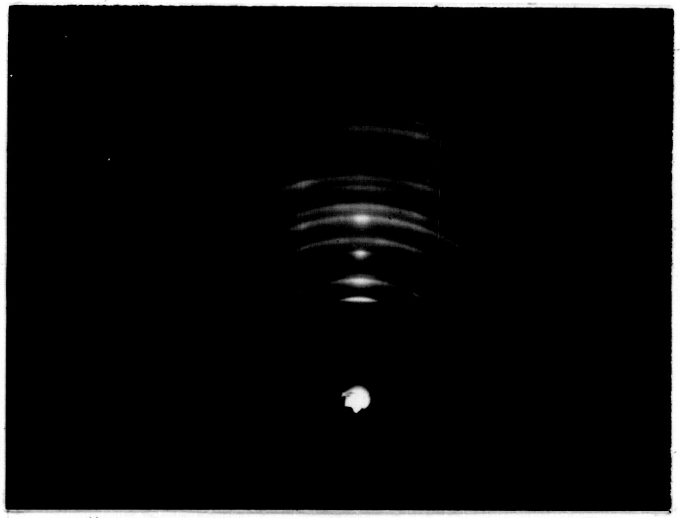

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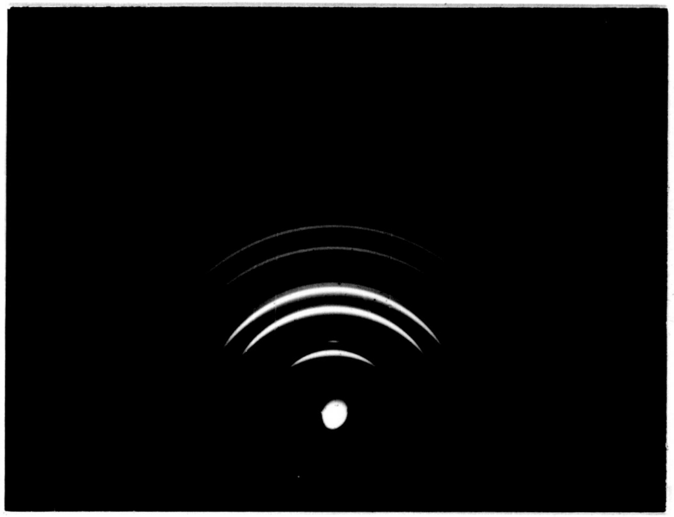

(B)

(D)